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APPARENT ANOMALY IN FREEZING OF ORDINARY WATER, (U)
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*Apparent anomaly in
freezing of ordinary water*

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*Cover: Superimposition of a series of timed photographs
obtained for basic freezing rate measurements.
(Photograph by George Swinzow.)*

CRREL Report 76-20

Apparent anomaly in freezing of ordinary water

George K. Swinzow

June 1976

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CRREL Report 78-20

Freezing of ordinary water
in various amounts in

George F. Swenson

June 1978

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Under ordinary conditions, the freezing of water begins with supercooling and ice nucleation, and proceeds at 0°C at the ice/water interface until ice formation stops. The presence of solutes, high pressure, or dispersal in fine pores causes the water to freeze at temperatures below 0°C (the so-called freezing point depression). Whenever freezing begins, it proceeds at a constant temperature, or at a temperature which becomes progressively lower. A temperature rise during ice formation is considered here to be an anomaly. Under all equal circumstances, the conditions under which an anomalous freezing temperature is observable appear to be very special. This report describes two different experiments displaying the anomalous rise of temperature after nucleation and during ice formation. In one case the water was dispersed in the fine pores of fine powders; in the other case pure water was frozen in a transparent insulated cell. Photographic observations were made; relations of ice surface to water volume were measured.		

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PREFACE

This report was prepared by Dr. George K. Swinzow, Geologist, Construction Engineering Research Branch, Experimental Engineering Division, U.S. Army Cold Regions Research and Engineering Laboratory. The work presented in this paper was supported under DA Project 4A061101A91D *In-House Laboratory Independent Research, Task 03, Work Unit 132*. The able laboratory assistance of Dennis Farrell, Mechanical Engineer, USA CRREL, is acknowledged.

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CONTENTS

	Page
Abstract	i
Preface	ii
Conversion factors for U.S. customary and SI units	iv
Introduction	1
Materials, instruments, measurements	2
Experiments with water freezing in fine pores	6
Freezing experiments with bulk water	9
Summary and conclusions	19
Literature cited	23

ILLUSTRATIONS

Figure

1. The freezing of saturated silica powder, time-temperature relation	2
2. Specimen arrangement	4
3. Constant temperature cabinet	5
4. The freezing of an inert quartz-water mixture, 100% saturated	7
5. Time vs temperature record of freezing quartz powder	8
6. Controlled freezing experiment, schematic illustration	10
7. Recorder chart of a freezing experiment	11
8. Dissipation of dye streaks in the freezing vessel	12
9. Temperature measurements within convection cells	13
10. Convection in the process of freezing	15
11. A superimposition of a series of timed photographs obtained for basic rate measurements	15
12. Water and ice temperatures during freezing experiments with a constant rate of ice advance	16
13. Ice/water interface vs time	17
14. Water volume vs time	18
15. Water volume vs ice surface	18
16. Ice surface to water volume vs time	18
17. A discontinued experiment in polarized light	19
18. The appearance of a normal sequence of events during an acceptable experi- ment in partially polarized light	20
19. The final appearance of the freezing experiment in polarized light	21
20. Maxwellian distribution	22

TABLES

Table

I. Material sizes used in freezing experiment	3
II. Freezing experiments on fine powders	7

CONVERSION FACTORS FOR U.S. CUSTOMARY AND SI UNITS

<i>Multiply</i>	<i>By</i>	<i>To obtain</i>
Degrees Celsius	$(1.8 \times ^\circ\text{C}) + 32$	Degrees Fahrenheit
Calorie (thermochemical)	4184.0	Joule
Gram	0.0022	Pound (avoirdupois)
Centimeter	0.394	Inch
Micrometer	0.000039	Inch

APPARENT ANOMALY IN FREEZING OF ORDINARY WATER

George K. Swinzow

INTRODUCTION

The equilibrium temperature of water and ice under standard conditions is zero degrees Celsius (0°C). To freeze a discrete amount of water, it must be placed in an environment with a temperature below 0°C and with the capability of removing all the latent heat of fusion (approximately 80 cal/g of water) together with its sensible heat (roughly 1 cal/g per degree) and still be below 0°C . The time-temperature history of a typical laboratory experiment (for example 500 ml of water placed in a coldroom with a constant -5°C temperature) begins with rapid cooling, during which time the water may reach temperatures significantly below 0°C . In order for freezing to begin, nucleation must take place. Once ice begins to form, the water temperature in the vicinity of the water/ice interface rises relatively quickly to 0°C and, providing that the water does not contain appreciable amounts of dissolved impurities, stays at 0°C until all the water in the vicinity of the measuring point is converted to ice. Under these conditions the process of freezing is highly predictable although the onset of nucleation is unpredictable. Normally ice nucleation is initiated by discrete, small, solid impurity particles which are almost always present. The purer the water and the smaller the specimen, the lower will be the temperature at which water may begin to freeze (Dorsey 1948). This appears to result from a chance that a nucleating particle is either present or absent in the supercooled water.

There are three reasons why water under normal conditions will not freeze at 0°C . They are: 1) presence of dissolved matter, 2) confinement in a fine capillary, and 3) sufficiently high ambient pressure. The freezing of a salt solution may begin at a temperature below 0°C , and the lowering of temperature will be proportional to the "strength" (concentration) of the solution. Since ice does not form any solid solution (Ben-Naim 1974), the first ice crystals increase the concentration of the remaining solution which freezes at a progressively lower temperature. Since the grain surfaces of most common soil minerals are leachable (partially dissolvable), the moisture in most soils is a solution. Thus the freezing of soil moisture is in principle indistinguishable from the freezing of a salt solution (Fig. 1). In some special instances when a fine material is unleachable, it freezes when saturated with water in a manner similar to pure water: at a constant but lower than 0°C temperature. Water under high pressure freezes at a low but constant temperature if the pressure is constant. Water in a vessel freezing from the outside inward may develop considerable destructive pressures.

There is no apparent reason why in the process of freezing the temperature may rise, instead of being constant or declining gradually, as shown in Figure 1. Nevertheless, temperature rises have been observed during freezing. In all cases in the past, such observations were dismissed and considered spurious, since often the magnitudes observed were less than the probable error of the temperature-measuring device.

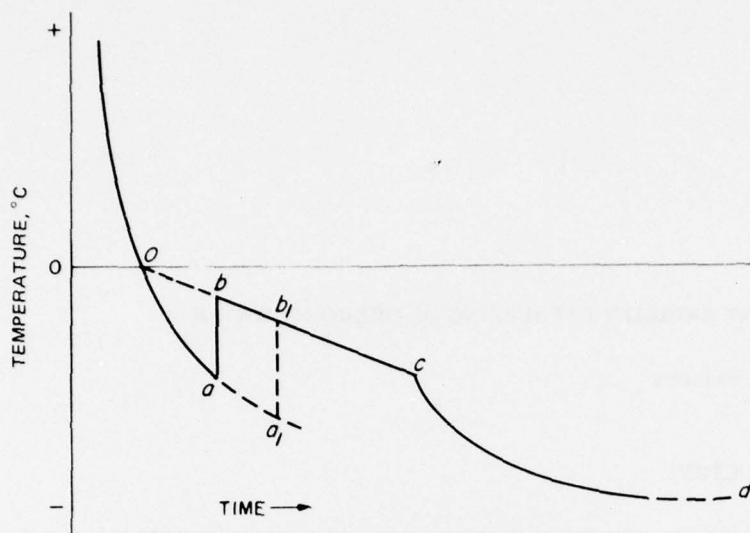


Figure 1. The freezing of saturated silica powder, time-temperature relation, where *a* is the nucleation point, *b* the beginning of ice formation, *c* the completion of ice formation, and *d* the ambient temperature. If freezing begins at *a*₁, the temperature rises to *b*₁.

At present, however, thermometric equipment an order of magnitude more sensitive than that available in the past may be used, and such observations can no longer be so easily dismissed. This report presents the results of two sets of experiments demonstrating temperature rises during the freezing process and gives a tentative explanation of the phenomenon.

MATERIALS, INSTRUMENTS, MEASUREMENTS

Since it was to be expected that water in fine pores would freeze at a temperature distinctly below 0°C, water was dispersed in the fine pores of a uniform powdery inert material. "Inert" meant, in this experiment, the properties of stability and resistance to leaching by ordinary water, and a very simple but sensitive test of acceptability of the trial powders was developed. A material, for example ordinary glass powder, was saturated with distilled water and stored typically for 48 hours; a water specimen was then centrifuged from the material. Drops of water from mixtures of soluble powders when evaporated on a microscope slide show characteristically an amorphous precipitate (this is a method commonly used in microchemistry). Thus, if the water from the pores of a glass powder showed such a precipitate, then the glass powder would be unacceptable.

Size uniformity was also desirable since it provided control of the degree of saturation, specific surface, etc. The abrasives industry produces a large variety of powders and several were tested for acceptability. Commercial alumina abrasives were found to be unacceptable because of their instability, but materials such as commercial corundum powder, ground quartz and feldspar (albite) resisted leaching, and were acceptable. The crushing and grinding of such materials as quartz or feldspar produces, however, a mixture of particles differing in size and shape, and routine screening was not found to differentiate them adequately. Settling fine particles in a simple cascading flow system (Vanderwilt 1938) was found to result in materials with high uniformity. For coarse

fractions a solution of an ordinary commercial thickener was used; the increased viscosity of the water permitted settling of uniform fractions.

Normally the "size" of a powder is designated by a numerical rating which equals half the sum of two nominal sieve opening sizes between which the powder is retained. The term "size" of a powder in this report is defined differently; it is half the sum of two mutually perpendicular dimensions as measured on the microscope stage. Two techniques were used to find powder size: direct measurement in vertical parallel light of the powder on a microscope slide with micrometer measurements (which was found to be sufficient for coarser material) and microphoto enlargement (empty magnification) which was necessary for fine particles. Due to the cascade settling in water, a very good uniformity of shape was noted; the ratio of width to length never exceeded 1/1.2, which shows the degree of the grains' sphericity (roundness varied with the fracture habits of the particular minerals). This degree of shape uniformity could not have been achieved by conventional fraction separating methods. Materials selected for the experiments are listed in Table I; certain other intermediate powders were set aside for uses as described below.

Table I. Material sizes used in freezing experiment.

<i>Size measured (μm)</i>	<i>Largest observable variation</i>	
	<i>($\pm \mu\text{m}$)</i>	<i>($\pm \%$)</i>
580	2.6	>1
420	2.4	<1
200	2.3	<2
135	2.6	>2
64	2.5	<4
42	2.2	<5
64	2.5	<4
20	2.0	20
13	1.6	25
4	0.6	15
2	0.3	30

The greater the degree of uniformity in the size, shape and physical properties of the surface of the materials, the better results are obtained in uniformity of packing (density, porosity and moisture content) if packing is done uniformly. Dalla-Valle (1948) and Dersievicz (1958) investigated consistency of packing and found that assemblages of uniform materials pack consistently to a porosity of $40 \pm 3\%$.

The best reproducible results were obtained by settling and vibrating materials in air-free water. Excess water was removed by placing a dry powder of a slightly larger size on top and in contact with the material settled in the container. By capillary action excess water moved out and the specimen remained saturated in its densest state. By this method the saturated state with the densest possible packing could always be reproduced. Control was performed by routine moisture content determination and picnometric determination of specific gravity.

The specimen arrangement is shown in Figure 2. Since there was concern about asymmetric and irregular heat flow, a series of fine thermocouples were used in separate trials, and it was found that heat flow was sufficiently symmetrical from the center outward.

It is evident that water dispersed in the pores of a uniform fine powder will freeze differently than in bulk: the volumetric heat of fusion will be only that of the water in the pore space, and

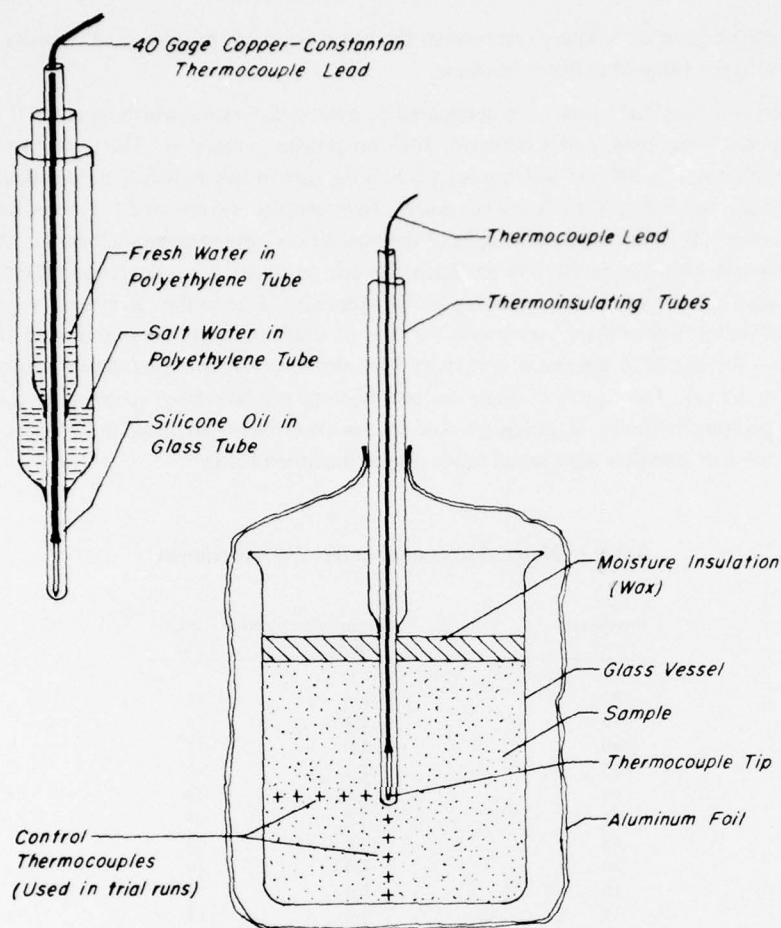
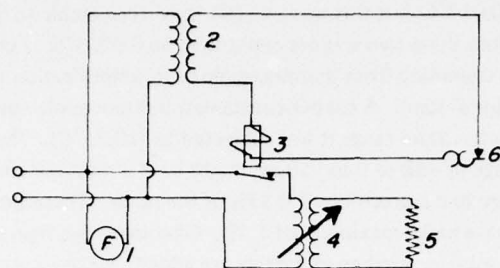


Figure 2. Specimen arrangement.

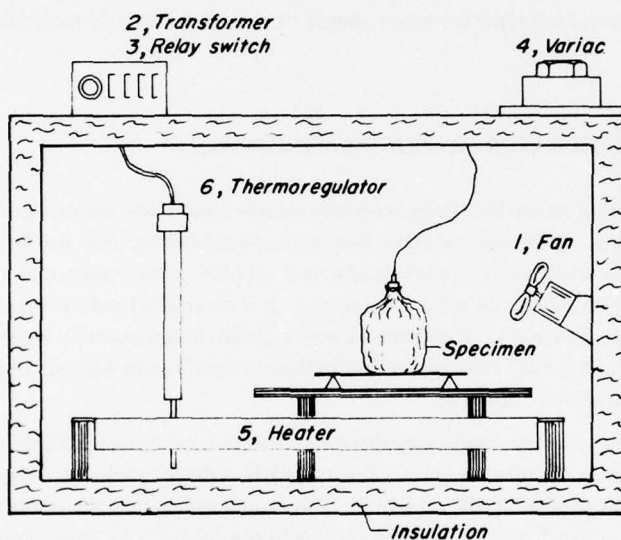
the specific heat of a water-saturated quartz powder will be, at 40% porosity, approximately $0.69 \text{ cal/cm}^3 \text{ } ^\circ\text{C}$. This modifies the shape of the time-temperature graph; compared with an equal volume of water such a mixture will cool down faster and the plateau of ice formation will be shorter. This, and the fact that the experimental specimens were relatively clean, required measures to avoid excessive supercooling.

Two methods of eliminating undesirably large degrees of supercooling were employed. The first consisted of placing into the specimen a drop of water containing nuclei (which can be defined only as impurities with the capability to nucleate freezing) which triggered freezing as soon as the specimen temperature went below 0°C . The method worked by initiating freezing at the desired spot and at the desired temperature, but was unacceptable, since no matter how small the drop of water, it was always contaminating. Another method was safer. It consisted of placing a very thin, flexible water-filled capillary into the spot where the beginning of freezing was desired. When the desired temperature below freezing was reached, nucleation was initiated through the capillary by bringing its free end into contact with ice.

Freezing took place in a thermostatically regulated cabinet at -1°C with a measurable variation of $\pm 0.03^\circ\text{C}$. The thermostatic regulator was a normally open mercury expansion device, regulating



WIRING DIAGRAM



CABINET INTERIOR

Figure 3. Constant temperature cabinet.

heat, which provided more accurate temperature stability than regulating refrigeration. Accordingly, as with a biological incubator, the cabinet had to be placed in a lower ambient temperature than its setting, and so it was placed in a coldroom with a -5°C temperature. As a measure of the cabinet's performance we can state that there were no observable temperature deviations inside a frozen specimen of saturated sand used in the trials after it reached thermal equilibrium. The arrangement is shown in Figure 3 (the sand was used only to test the cabinet).

Special attention was given to preparation of thermocouple junctions. Thermocouple measuring points were soldered the routine way, then kept for 20 min at a temperature just below that of melting solder and tested for stability and reproducibility of temperature measurements. Normally, of 10 to 12 soldered points, only 2 or 3 could be accepted. Another consideration was given to the validity of the measurements performed: the copper-constantan thermocouples may have introduced a maximum error of $\pm 0.0005^{\circ}\text{C}$ when using a $\pm 0.25^{\circ}\text{C}$ scale. This error appears systematically in each measurement, and although its maximum range is known, its actual magnitude remains undetermined.

The signal amplification system had a zero position uncertainty of $\pm 0.5 \mu\text{v}$ which could result in a temperature error of $\pm 0.013^\circ\text{C}$, but this was a visible error correctable to $\pm 0.005^\circ\text{C}$. The total maximum accuracy error from these two sources could then be 0.0055°C . Furthermore, one had to consider precision errors stemming from thermocouple drift, amplification response and limits of sensitivity in the measuring system. A copper-constantan thermocouple could have its output changed by 0.75% in the temperature range it was subjected to ($\pm 0.25^\circ\text{C}$). The signal amplifier, within the experimental range of +50 to 0 to $-50 \mu\text{v}$, might have a response change of as much as $\pm 0.4\%$. The recording system had a precision of 0.35% of the range. Therefore, the total errors in precision are estimated to have had a maximum of 1.5%. Of course, this figure indicates the maximum theoretically possible total error when all factors are added. Since all errors discussed might have either positive or negative values and might not always occur at their full values, and since all measurements were repeated a large number of times, most errors were probably much smaller. Therefore, the observations reported below should be considered as valid to a high degree of certainty.

EXPERIMENTS WITH WATER FREEZING IN FINE PORES

From the foregoing we see that there is no conceivable reason why the process of freezing might or could take place at a temperature higher than that of equilibrium. It is also hard to visualize any reason why an initially low equilibrium temperature (due to the presence of a solute, or constant high pressure or dispersion in fine pores) would rise. It is especially hard to visualize the rise of the freezing temperature above 0°C . Experiments with a phase change anomaly would, one would think, be best performed at a temperature below that of normal equilibrium without an increased pressure or the addition of a soluble substance.

This consideration was the reason why the water for the freezing experiments was dispersed uniformly in the pores of uniform, unleachable materials as described above. The size of the specimen and the amount of insulation around it were adjusted so that the whole cycle — cooling, supercooling, nucleation, freezing, and final cooling to the cabinet's ambient temperature — took place in three to six hours. The centrally located thermocouple with the special heat leak prevention measures (shown in Fig. 2) recorded the time-temperature sequence of the process within the accuracy and precision described.

In essence, the observations showed a small temperature rise after supercooling and nucleation during the freezing stage. Figure 4 shows the observations in a schematic way. A specimen, initially at an above-freezing temperature, loses heat and supercools, i.e. reaches a negative temperature. At a point *a* in Figure 4 either spontaneous or artificial nucleation takes place. At this point in a very short time (recording equipment shows no time) the temperature reaches point *b*, which is by definition the onset of freezing. If: 1) the initial volume of water is large enough (about 1 cm^3 or more) so that no appreciable surface tension effects take place, and 2) the water is pure enough that there are no measurable solute effects, this temperature is 0°C . For water in very fine pores, capillaries or single droplets, point *b* is below 0°C . Point *c* in Figure 4 is where ice formation is complete and the specimen cools and asymptotically reaches the ambient temperature.

Normally, most of the path between *b* and *c* is a straight line (the break at *c* is very difficult to observe), but the observed effect consisted of a slight rise of temperature while the process of ice formation was underway (point *b₁* in Fig. 4).

Figure 5 is a reproduction from a time-temperature recorder strip showing an actual measurement obtained. A series of trials was made to see whether or not there is a relation between the rate of freezing, grain size, ambient temperature and magnitude of the temperature rise.

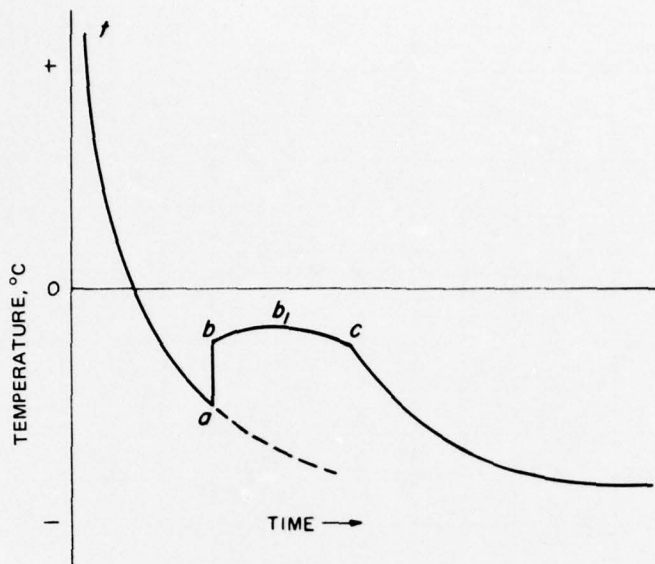
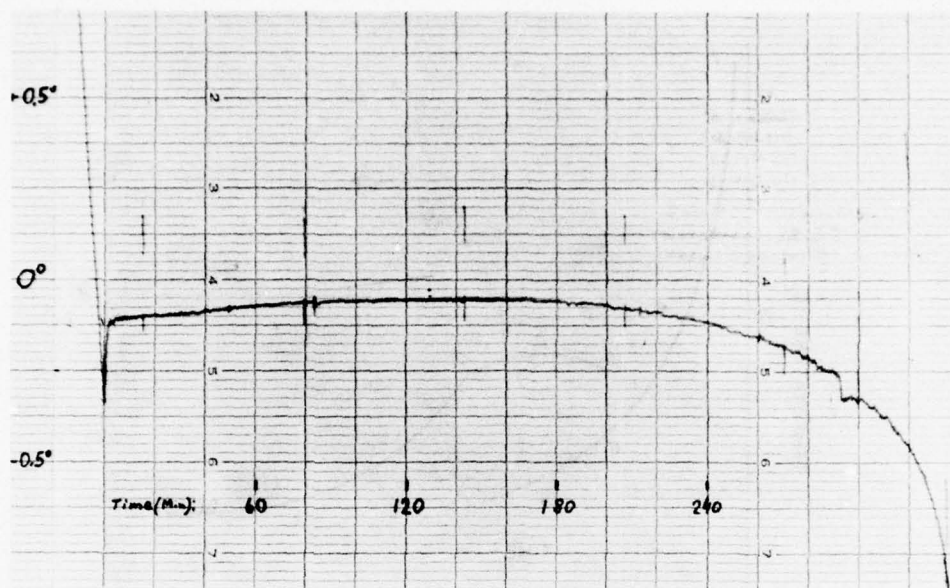


Figure 4. The freezing of an inert quartz-water mixture, 100% saturated, where *a* is the nucleation point, *b* the beginning of ice formation, *b₁* the peak temperature during freezing, and *c* the completion of ice formation.

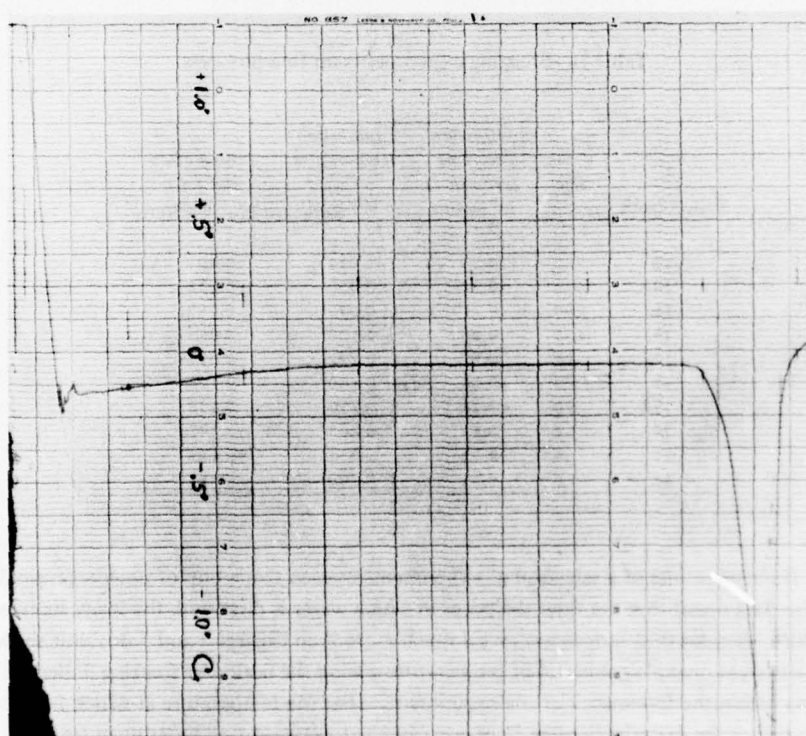
Table II. Freezing experiments on fine powders.

Specimen	Grain size (μm)	Moisture content (saturated) by weight	Equilibrium temperature (°C) (<i>b</i> in Fig. 4)	Temperature rise (°C) (<i>b-b_a</i> in Fig. 4)
13	580	0.23	0.012	0.007
14A	420	0.22	0.050	0.038
15	200	0.21	0.077	0.052
16	135	0.20	0.100	0.070
16E	64	0.22	0.122	0.077
17	42	0.21	0.150	0.105
17B	20	0.21	0.170	0.125
20	13	0.21	0.205	0.145
21	4	0.22	0.255	0.185
22	2	0.21	0.270	0.195

Table II shows results of a selection of experiments in each size group of powders from 580 to 2 μm. The data reveal that the finer the pores in which water is dispersed, the lower its freezing temperature. Besides this, it does not reveal much more than Figures 4 and 5 do; all it shows is that there is a yet unexplainable rise of temperature during the period of freezing under the special conditions within the framework of the experiment. That the temperature at which freezing began became lower as the material became finer was expected; water in fine pores must freeze at a lower temperature (an analogy is the freezing of fine drops of water). Since the anomaly in the temperature observed was connected with heat, whether generated, released or otherwise induced at the measuring point, there was a need for explanation or, to go a step further, for experiments capable



a. Spontaneous nucleation.



b. Artificial nucleation.

Figure 5. Time (min) vs temperature (°C) record of freezing quartz powder.

of being explained. The higher rise in temperature (Table II) with finer materials may only be the consequence of higher total interfacial heat flow resistance. And this means that the experiments cannot be explanatory; they are just a demonstration.

Other observations made in the process of experimental work concentrated mainly around the process of freezing, changes in the rate of freezing and moisture content.

When freezing was induced by artificial nucleation to proceed from the center outward, the phenomenon of temperature increase during phase change was not observable. The reason for this is obvious — heat was flowing out, without accumulation. If supercooling were allowed to reach very low temperatures at ambient temperatures significantly below -1°C (around -4° or -5°C) the phenomenon could not be observed and freezing proceeded rapidly with the specimen being part of its own heat sink. When specimens were loosely packed, with a water content higher than that of saturation in the densest state, the phenomenon of temperature increase during phase change again could not be observed. The specimens froze in a way similar to that shown schematically in Figure 1; i.e. the temperature during ice formation was steadily falling. The author noticed cracking and water extrusion; this led to the conclusion that pressure developed within the specimen and led to a lower freezing temperature.

It is concluded that the experiments described were an illustration of two simultaneous effects. These were the general lowering of equilibrium temperature of water when it was dispersed at freezing temperatures in fine inert media, which was studied in detail by Bakaiev et al. (1959), and the unexplained rise in the equilibrium temperature when phase change took place. Since there was no conceivable heat source for this effect (freezing proceeded from the outside in, apparently without pressure buildup) the heat formation must have been related to the ice/water interface rather than the interfaces between water and mineral grains. For this reason a method of experimenting with pure water had to be designed.

FREEZING EXPERIMENTS WITH BULK WATER

The freezing of a volume of water from the outside inward results in a pressure buildup, with an inevitable lowering of equilibrium temperature. To avoid this effect one needs a reliable means to relieve the pressure. One way to do this is to have a small balloon inflated with air in the center of the water container. During freezing, such a balloon would take up most of the pressure developed. An exploratory experiment of this type was performed with approximately 5 l of water and several trials were made at -40°C . The very low temperature of -40°C was used to expedite the rate of freezing. A rise of temperature similar to that of the previous experiment could in some cases be observed, but electrical background noise, fluctuations in pressure, lack of control in freezing rates and perhaps the experiment's general crudeness led to the abandoning of any further work of this type.

To allow more control over the freezing process and to eliminate as many as possible of the variable unknowns (such as nonlinearity of freezing at a constant temperature, asymmetric ice advance toward the center, etc.) a new experiment was designed. A $2\frac{1}{2}$ -cm-thick aluminum plate was cut out in the center and sandwiched between two thermoinsulating windows (two air spaces for each) so that a rectangular vessel of approximately 750 cm^3 was formed. Adjacent to the cavity a 1.4-cm-diam U-shaped canal was drilled for circulation of coolant. Figure 6 shows schematically the experimental arrangement.

The thermistor probe in the center of the cavity was inserted through an opening in the aluminum which also served to fill the cavity with water and to relieve the pressure by removing by suction excess water during freezing. A thermocouple was used to monitor the temperature at the ice/aluminum interface, while the thermistor probe recorded the temperature in the center of the cavity. The

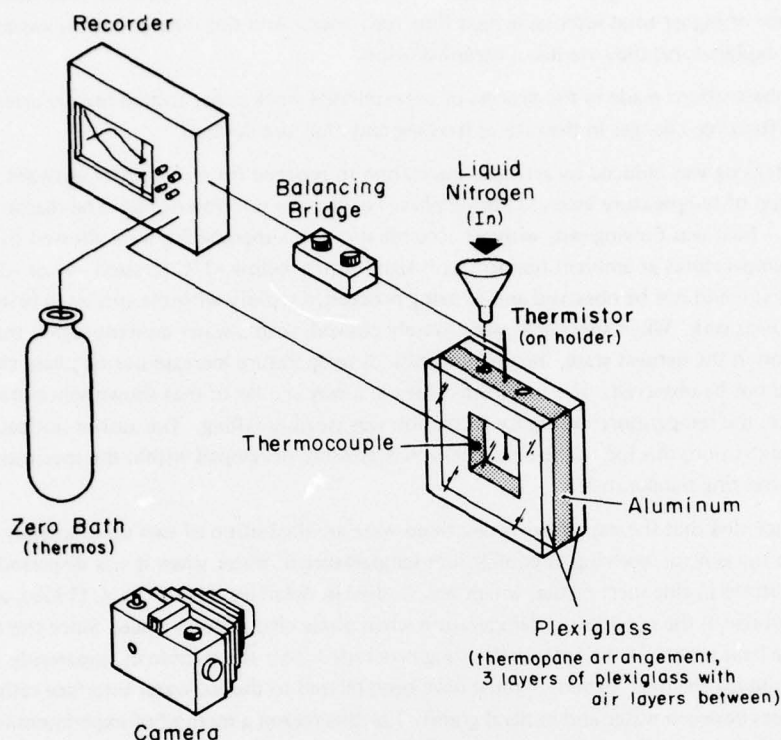


Figure 6. Controlled freezing experiment, schematic illustration.

sensitivity of the thermistor was sufficient to register a temperature difference of $\pm 0.005^\circ\text{C}$ or better, but only changes of $\pm 0.01^\circ\text{C}$ were recorded, which appeared sufficient for this series of experiments. Another thermistor probe was installed in a way permitting the exploration of temperatures in various parts of the cavity during freezing. The rate of freezing was controlled by the rate of coolant flow; the rate of the ice/water interface advance was determined from a series of photographs taken during the process of freezing.

The access port in the top of the cavity (not shown in Figure 6) was frozen over with a thin crust of ice at all times during the experiment. Excess water (from freezing) which was squeezed on top of the ice crust was siphoned off, so that there was never excess pressure developing. The freezing process could, therefore, be controlled at all times, and freezing rates could be kept constant. One specific situation of significance must, however, be pointed out. The formation of a single ice crystal and its growth after nucleation is normally accompanied by a continuous *increase* of the ice/water interface, and directional freezing, such as that in nature (from the top down), takes place with a *constant* ice/water interface. In the experiment about to be described, however, freezing from the outside in is accompanied by a progressively *decreasing* interface. This point is of importance for further considerations.

The experiments with the device shown in Figure 6 always began by storing it empty in a -5°C coldroom for at least 24 hours, so that the thermoinsulating window spaces lost enough heat to stay below 0°C for the duration of the tests. The actual work began by filling the cavity with cold water and circulating the coolant through the U-shaped canal. The preparation of relatively cold clean water presented certain difficulties. Percolating distilled water through a layer of crushed ice was unsatisfactory, since the water obtained was usually $0.2^\circ\text{--}0.3^\circ\text{C}$ above freezing. It was found that

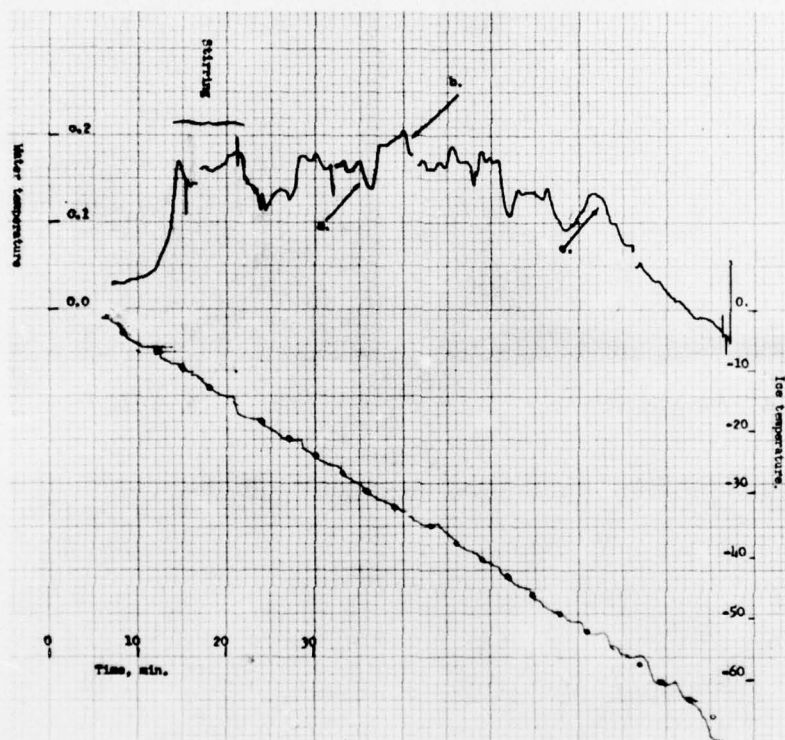
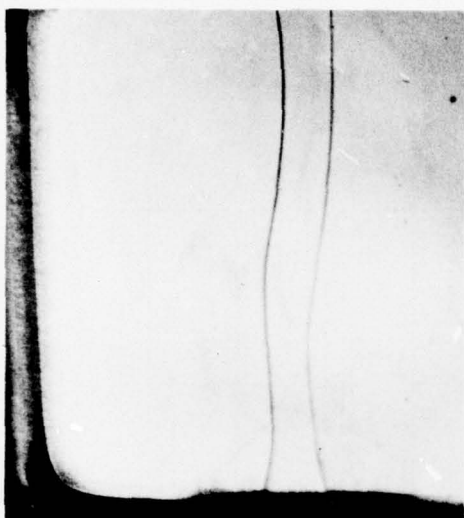


Figure 7. Recorder chart of a freezing experiment. Left scale, upper graph: water temperatures ($^{\circ}\text{C}$) in various parts of the vessel. Right scale, lower graph: temperatures at outer boundary of ice. Bottom scale: time (min).

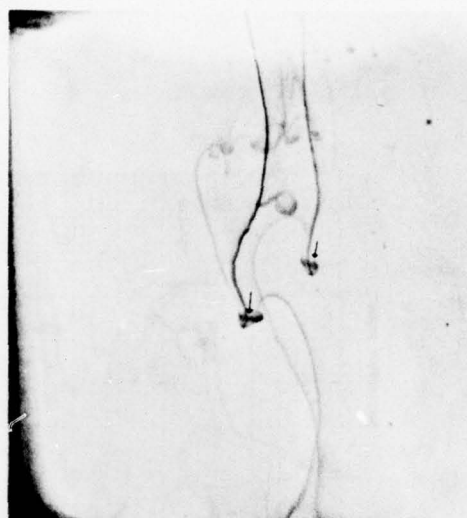
storing a supply of water overnight in a coldroom, during which time ice formed on the walls of the vessel, frequently resulted in "warm" water up to a half degree above freezing. The best procedure to avoid this was to use slightly supercooled water, which after being poured into the cavity formed some small ice crystals that rose to the top. This water had a temperature of only $0.02^{\circ}\text{--}0.03^{\circ}\text{C}$.

The actual experiment began by circulating liquid nitrogen and recording temperatures inside the vessel and at a side wall on the ice-metal contact (Fig. 6). The rate of temperature lowering at the ice-metal edge was kept linear by adjusting the coolant flow. The temperature in the center of the vessel was observed to rise noticeably during the first half of the experiment. Figure 7 is a simultaneous recording of the edge temperature and the water temperature, the latter obtained with a thermistor mounted so that it could be placed in various parts of the vessel. It was found that the water was by no means isothermal throughout the chamber.

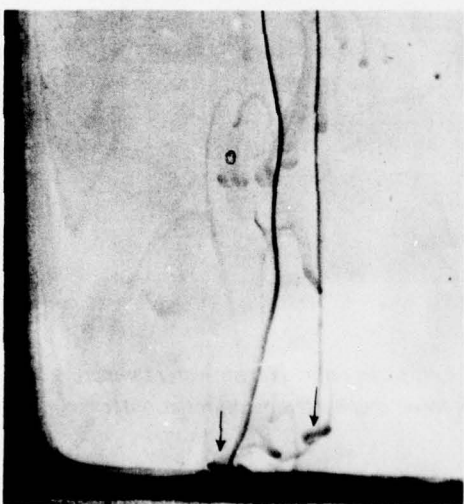
To see whether or not the slight disturbance introduced by thermistor movement inside the vessel interfered with the heat accumulation, the water was stirred in one experiment. It was noted that



a. 1 min after marking.



b. 3 min.



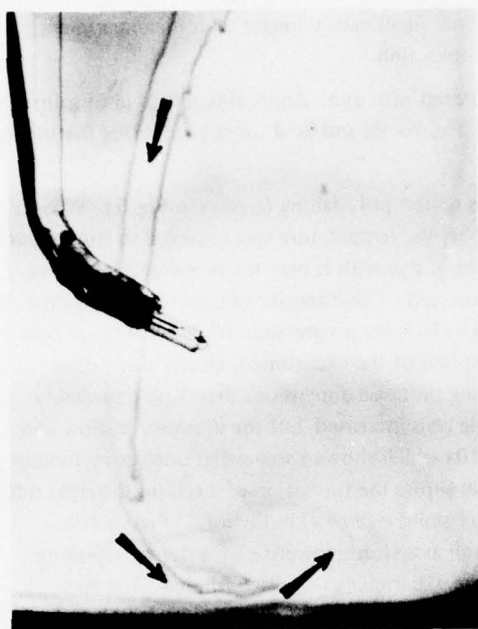
c. 4 min.



d. 5 min.

Figure 8. Dissipation of dye (KMnO_4) streaks in the freezing vessel.

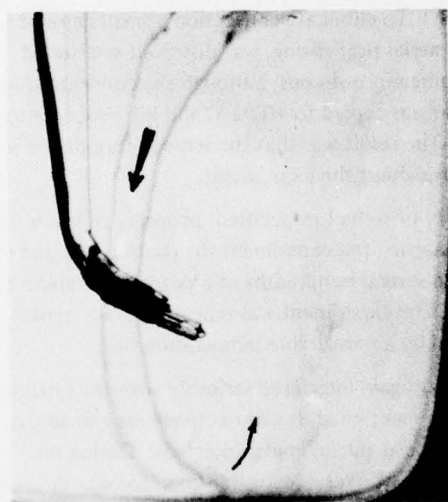
intermittent periods of stirring for 10 min resulted in a slight thermal disturbance, but the general rise in temperature continued. It was observed that the water in the experimental vessel showed perceptible convection movement. To visualize this phenomenon the water was marked by dropping two grains of potassium permanganate, which left two vertical lines in the reservoir (Fig. 8a). The crystal fragments rapidly froze into the advancing ice at the bottom and did not produce additional color in the water in the container. A curious phenomenon was observed within a few minutes (shown by arrows in Figures 8b and 8c): the streaks, originally linear, began to develop reverse plumes which settled within 2 to 3 min to the bottom. The remaining permanganate streaks broke



a. 3 min after beginning.



b. 3.5 min.



c. 5 min.



d. 8 min.

Figure 9. Temperature measurements within convection cells. (Dye is 20% alcohol and water solution added to aniline.)

up, forming many small cells and shear streaks (arrows in Fig. 8d). Apparently due to the solution's density, crystalline potassium permanganate is not a suitable material for decorating convection motion. An attempt to use aniline dye solution in water also failed, presumably because the solution was heavier than water. An alcohol solution of aniline was, however, lighter than water. It was found that 20% alcohol added to an aniline water solution, if introduced with a syringe into a container of

isothermal water, stays in a motionless cloud for a time significantly longer than the experiment may last. This solution was used to help decorate convection.

Figure 9 shows closeups of convection cells decorated with dye. Approximately $\frac{1}{4}$ μ l of solution was introduced with a microsyringe into the water. Figures 9a and 9c show the exploring thermistor probe within an upward moving cell.

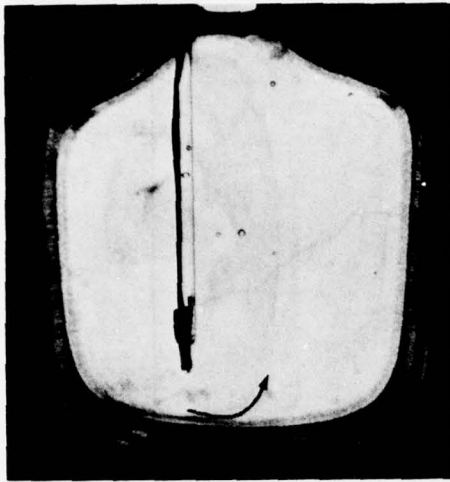
The temperature as observed on the recorder was temporarily falling (arrows in Fig. 7). When a downward-moving convection plume passed the probe, the temperature was observed to rise. Figure 9b shows a confluent stream of water moving a cloud of dye with it over the probe and 9d shows the forming of a counterclockwise rotating convection cell. The intensity of convection, together with its pattern, changed in the ever-shrinking space as freezing progressed. While convection cells formed, moved and then disappeared during the first half of the experiment, clearly discernible double cells formed during the second part of freezing (in three dimensions they would probably be described as toroidal). The stability of the double cells increased, but the intensity of flow and temperature decreased. This can be seen in Figure 10a which shows a somewhat unclear asymmetrical convection cell in the left part of the picture; 10b shows the formation of a cell on the right side. The photograph was taken approximately 5 min after point c (arrow) in Figure 7. Figure 10c appears to show a slowing down of convection, as well as a steady lowering of water temperature. Figure 10d was taken approximately 5 min before the experiment was discontinued. The two arrows on the right side of Figure 10b indicate an intriguing phenomenon which was very often observable: the shear motion of water along the interface of the ice.

Since convection is a process of thermal mixing, there arises a question: What would be the thermal history of the water without any convection? To eliminate convection a small amount of industrial water thickener, the type used in modern aerial firefighting, was dissolved in distilled water. When this thickener was used the water became more viscous, although the concentration of the suspension was less than 0.01%. This solution was cooled to $+0.02^{\circ}\text{C}$ and introduced into the vessel, and the experiment proceeded as described. The result was that the temperature of the water did not rise, but fell to 0°C and remained at 0°C throughout the experiment.

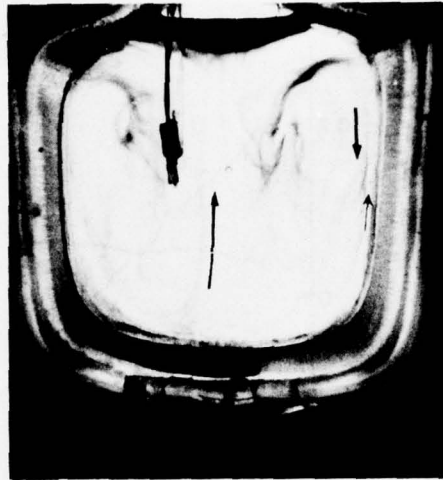
Another exploratory test concerned the possibility of some (unspecified) property of water which causes temperature rise at freezing. It consisted of starting the experiment the routine way and removing all remaining water after its temperature rose several hundredths of a degree and replacing it with new water chilled to the initial temperature. The experiment was repeated several times with the result that freezing was always accompanied by a measurable temperature rise.

Neither stirring nor removing the water and starting again interfered seriously with the phenomenon of temperature rise in the process of freezing. As mentioned, it was relatively easy to adjust the coolant flow to a linear lowering of the temperature at the ice/metal interface. During the progress of freezing, the volume of water was decreasing, the total ice/water interface was shrinking and all geometric relations were changing. To obtain measurements of these changing relations, a continuous series of photographs from a fixed point was taken. A superimposition of photographic images taken at precisely known time intervals provided the basis for the necessary measurements (Fig. 11).

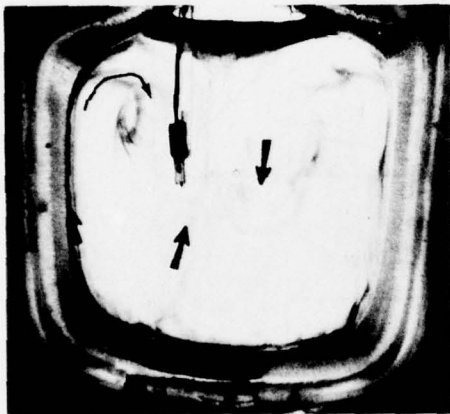
Three experiments were selected for acquisition of a set of data on the process of freezing (Fig. 12). The experiments lasted approximately 60, 80 and 110 min with deliberately linear chilling rates of 1.33°C , 0.75°C and $0.36^{\circ}\text{C}/\text{min}$. Temperatures were recorded from a centrally located stationary thermistor (due to pen leaks *a* and *c* had to be retraced on the same paper and *b* was a point-by-point redrawing). Since the stationary thermistor point encountered only a few strong convection fluctuations, the water temperature vs time plot of Figure 12c was exceptionally smooth. It should be recollected that Figure 7 was obtained from a mobile thermistor placed into visible



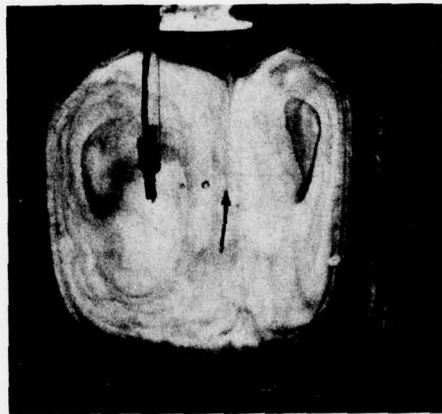
a. 60 min after beginning.



b. 64 min.



c. 69 min.



d. 74 min.

Figure 10. Convection in the process of freezing. The water motion slows down as temperature drops; convection cells are more discernible.

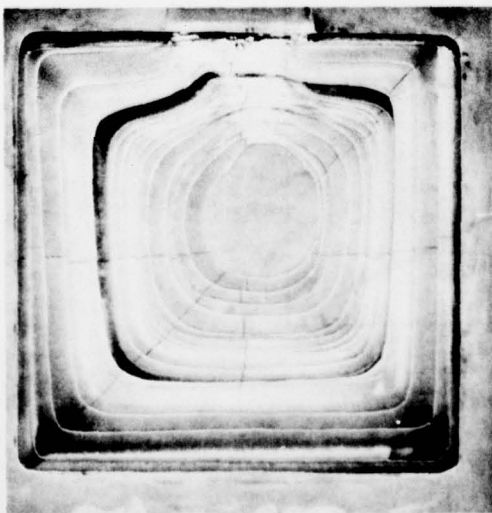
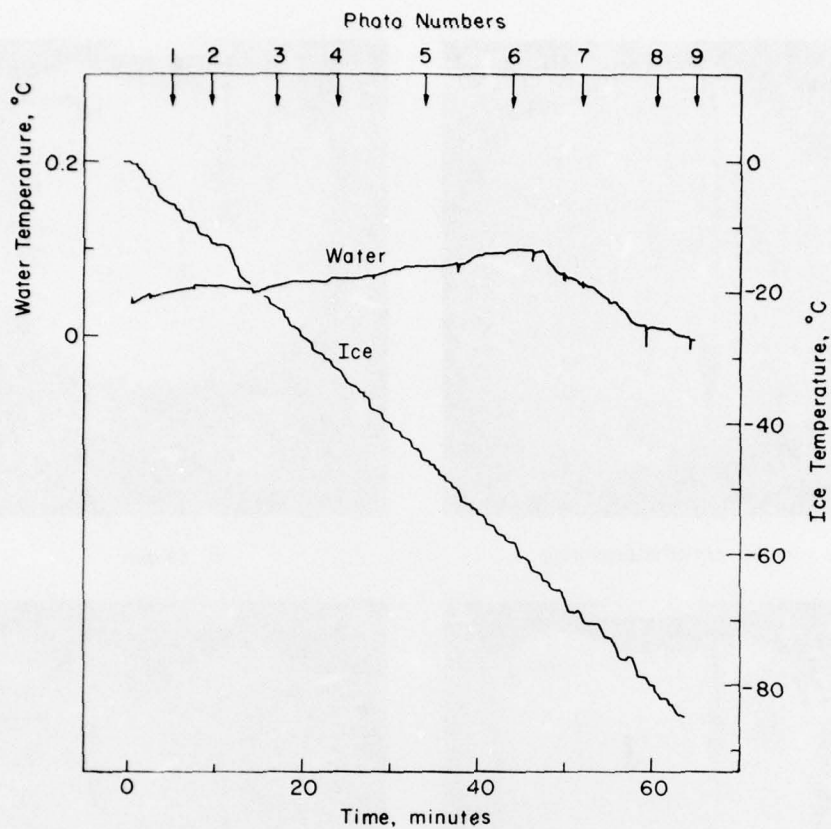
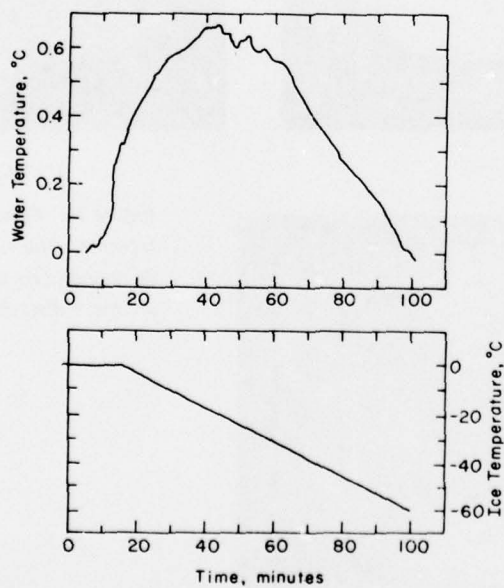


Figure 11. A superimposition of a series of timed photographs obtained for basic rate measurements.

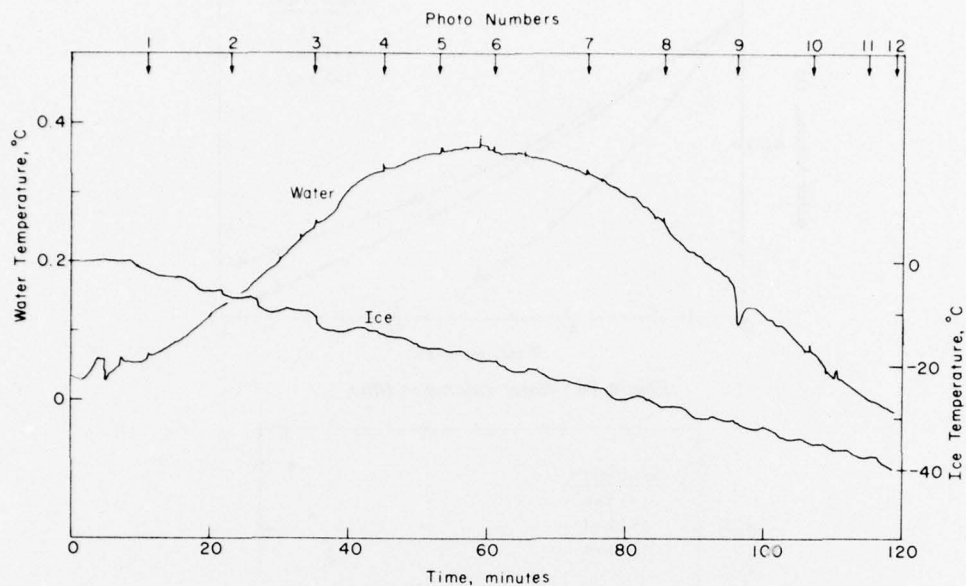


a. Cooling rate $1.33^{\circ}\text{C}/\text{min}$.



b. Cooling rate $0.75^{\circ}\text{C}/\text{min}$.

Figure 12. Water and ice temperatures during freezing experiments with a constant rate of ice advance.



c. Cooling rate $0.36^{\circ}\text{C}/\text{min}$. (The photo numbers in graph (c) correspond to contours in Fig. 11.)

Figure 12 (cont'd).

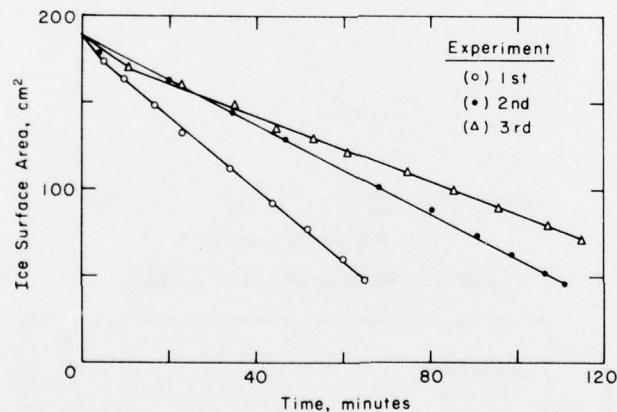


Figure 13. Ice/water interface vs time.

convection currents. The rapid down-dip in Figure 12c at 96 min was registered when the thermistor tip was submerged into a rising convection plume.

As mentioned, the ice/water interface, the water, and the ice volume, together with their ratios, change under the experimental conditions in a special way. The decrease of the ice surface proceeded nearly linearly with time (Fig. 13) as was expected. Water volume also decreased nearly linearly (Fig. 14). The relationships of surface to volume and surface/volume ratio to time are shown in Figures 15 and 16. Figures 13-16 show that with linear cooling of the ice the volumetric rate of freezing is nearly linear, while the ratio of the surface area of ice to the remaining volume of water increases with time.

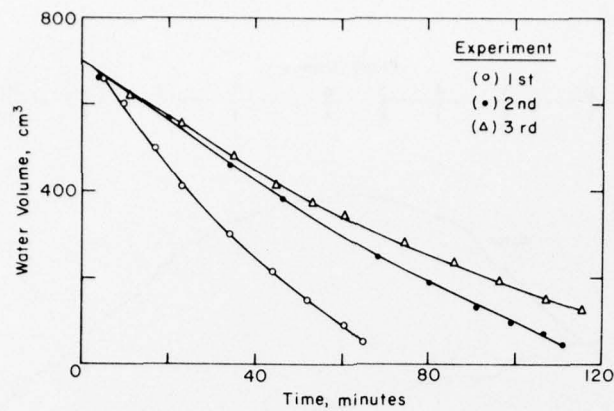


Figure 14. Water volume vs time.

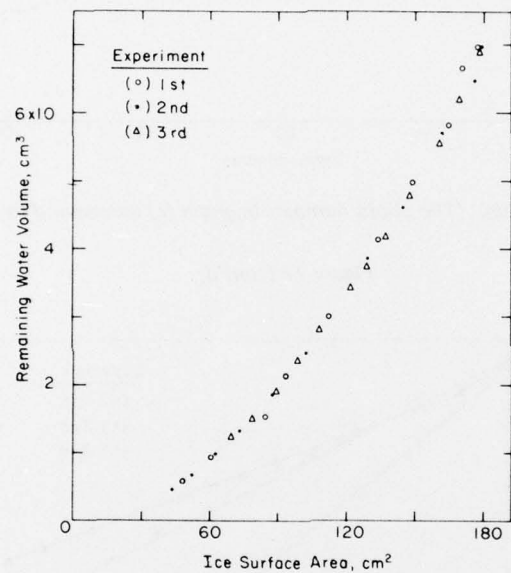


Figure 15. Water volume vs ice surface.

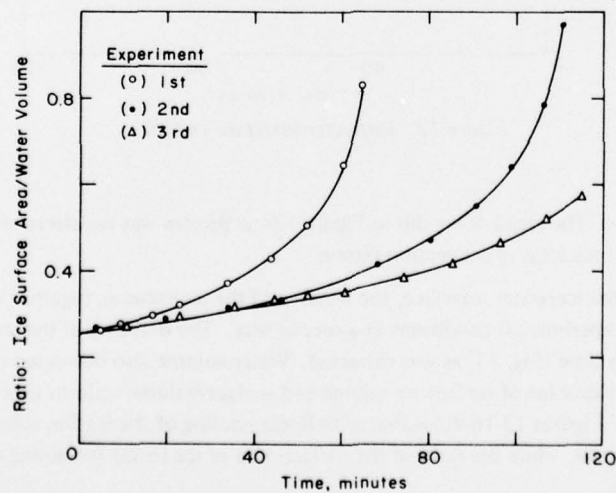


Figure 16. Ice surface to water volume vs time.

SUMMARY AND CONCLUSIONS

The effect of the temperature rise during freezing of ordinary water was observed and demonstrated by two different experiments. The first, consisting of the freezing of water dispersed in fine pores, demonstrated the effect only weakly. It required a large amount of sample preparation effort but did not have sufficient control over the process of freezing. The water was in intimate contact with mineral particles which, besides preventing a pressure buildup during freezing from the outside in, had a high heat conductivity and specific heat, thus diminishing the overall effect. The assumption that the temperature rise anomaly will take place only if the equilibrium temperature is depressed significantly below zero was found to be erroneous.

The search for better control and a better experimental principle led to the second arrangement (shown in Fig. 6) of experiments with pure water in a nearly two-dimensional set-up. The total magnitude of the temperature rise was observed to be larger, but no clear relation to freezing rate was observed. The technique of heat removal using boiling liquid nitrogen provided a positive control over the freezing process, and the use of more refined measuring techniques (thermistors) provided a higher degree of confidence. Another advantage of the experiments was the use of marker fluids to observe convection.

The effect, as observed on numerous occasions, was consistent. Removing the water after the initial rise of temperature and replacing it with freshly chilled water did not eliminate the effect, nor did stirring. As mentioned, a special precaution was taken to prevent heat influx into the chamber itself. This was achieved by storing it for at least a day in a coldroom at about -5°C . It was found that longer storage resulted in intensive ice needle formation on the inner surfaces of the insulating windows. The ice needles obstructed the view considerably, but it was observed that strong sheet convection was taking place parallel to the windows and the temperature inside the chamber rose rapidly and irregularly. This type of experiment (Fig. 17) had to be discarded. During an acceptable experiment the amount of ice forming on the windows was significantly less than 1% of the total ice surface (Fig. 18). But the presence of ice at the windows throughout the experiment and the



Figure 17. A discontinued experiment in polarized light.

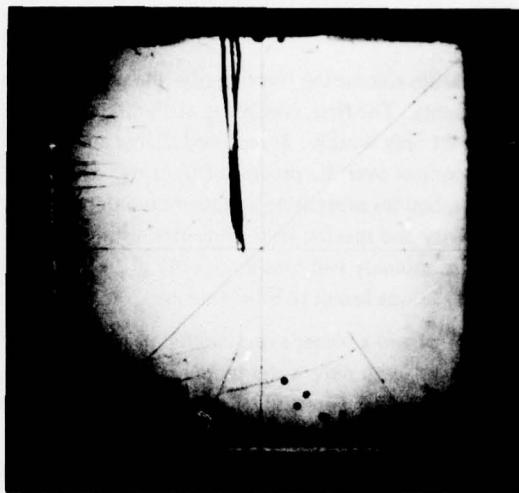


Figure 18. The appearance of a normal sequence of events during an acceptable experiment in partially polarized light.

relatively slow growth of its crystals were the reasons why heat influx into the water along the line of view was judged not to be a problem. Trials in a coldroom at a negative ($^{\circ}\text{C}$) temperature excluded heat influx completely and demonstrated the temperature rise. Also, a strong light beam focused on the thermistor tip did not produce any response on the recorder. The experiment was usually discontinued after a gradual temperature decrease down to 0°C . At that stage the appearance of the cavity was typically similar to that shown in Figure 19.

The scientific conception of an objective reality is by necessity always partial and incomplete. As much as it would have been desirable, the two series of experiments neither fully explored nor fully described the phenomenon of temperature rise accompanying phase change of ordinary water. Nevertheless, in both series this phenomenon was registered and observed. This was possible by the use of sufficiently sensitive measuring devices and by taking care to eliminate possible outside sources of heat. Otherwise the observations would have to be dismissed as spurious.

The second series of experiments, where freezing and therefore heat flow were essentially two-dimensional, had the advantage of sufficiently reliable temperature measurement techniques and ease of freezing rate control, but it was at the same time weak in the fact that the ice/water interface was ever-decreasing.

Our conception that the ice-water equilibrium temperature during freezing under standard conditions is fixed may be significantly complete, except that the concept of "temperature" as three-dimensional molecular vibration or motion breaks down at the two-dimensional nature of the interface. Not having a full and complete explanation for the described phenomenon a partial and tentative one is presented.

Brownian movement is present in gases and liquids. The kinetic theory is applicable to both a liquid and a gaseous state (Loeb 1962). Equilibrium may be regarded as a phase change dynamic state; i.e. at a solid/liquid interface an equilibrium state is a condition when an equal amount of matter (molecules) arrives and leaves the interface. Considering the danger of oversimplification we may also state that the temperature in a discrete volume of liquid (or gas) is the consequence of the

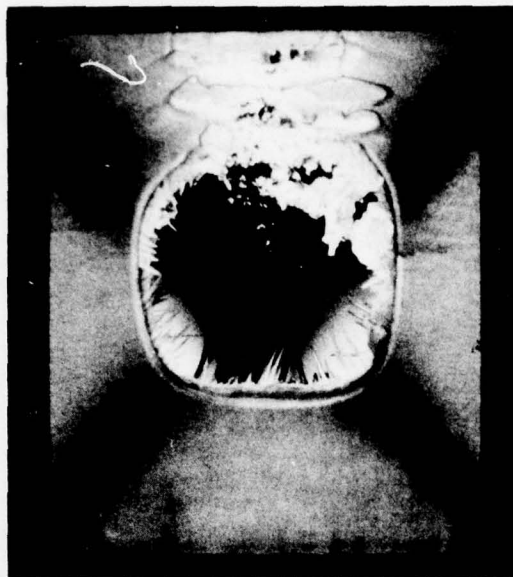


Figure 19. The final appearance of the freezing experiment in polarized light.

modal velocity or the modal translational energy of the molecules. The thermometer is then a large-scale integrating device presenting the overall energy content in the discrete volume, or rather the modal translational energy.

The view of a gas as an assembly of very fast, medium and slow molecules may, to an extent, be applied to liquids (Green 1952). The absolute temperature will have the following relation to the mean square molecular velocity:

$$C^2 = 3KT/m \quad (1)$$

where C^2 = mean square velocity

T = absolute temperature

K = Boltzmann's constant

m = mass of the molecule.

The concept of a discrete velocity as referred to a single molecule cannot be applied to liquids, since each molecule in its motion interacts necessarily with others. But, since both gases and liquids display Brownian movement, the Maxwell-Boltzmann distribution law may apply to both. Then, denoting the total number of molecules in the system by N and the representative motion by V , a form of the distribution law may appear thus:

$$\Delta N/N = (4h^3 \Delta V)/\pi^{1/2} V^2 C^{-h^2 V^2} \quad (2)$$

where h is a relation equal to $6.034 \times 10^7 (m/T)^{1/2}$; m and T are, as before, the molecular mass and the absolute temperature. Thus, the distribution law may be described in three simple terms:

$$\text{The modal speed of the molecules } V_m = 1/h. \quad (3)$$

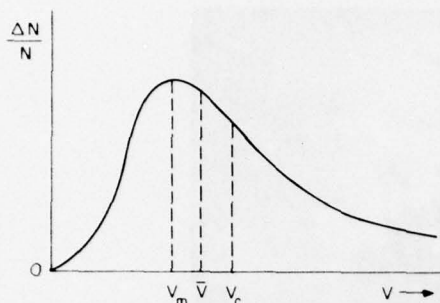


Figure 20. Maxwellian distribution, where V is velocity, N the number of molecules, V_m the modal speed of molecules, \bar{V} the mean speed, and V_c the effective speed of molecules.

The mean speed of the molecules $\bar{V} = 2/\sqrt{\pi h}$. (4)

The average kinetic energy $V_c = \sqrt{3/2 \times 1/h}$. (5)

(A graph representing the Maxwell-Boltzmann distribution law is shown in Figure 20.)

These three values described the well-known graph illustration of the distribution law. We must reemphasize that each numerical plot of N against V is representing only one specific energy state. Adding energy in the form of heat will move the peak of the distribution curve along the abscissa toward higher values of V . The position of the peak is, therefore, a consequence of temperature, and the temperature of a system depends upon the modal distribution of velocity of all the slow and fast molecules present.

The kinetic picture of a two-phase equilibrium is that of a constant molecule exchange between the gas phase and the liquid. There is no reason why a solid/liquid interface equilibrium state could not be visualized the same way. It is useful to have a brief glimpse at some differences of property and state found on both sides of an interface: the liquid molecules have thermal vibration and are subject to Brownian movement; solid crystalline molecules vibrate around fixed points (diffusively arranged structure). As a consequence there are the thermodynamic differences such as specific heat, heat conductivity, etc. The specific heat of ice is roughly half that of water, and so is its thermal conductivity.

Removal of heat from the interface into the ice results in the advance of heat into the water, and if the liquid phase is isothermal, there is no reason why a temperature rise should take place, except that the interface is confronted not with molecules of equal energy (speed) but with a variety of molecular energies. If the kinetic theory applies to liquids, then the ice/water interface will "immobilize" preferentially slower molecules; i.e. it will have less energetic molecules. Consequently, the water in the vicinity of the interface will be gradually enriched with fast molecules, and this is manifested in a shift of the distribution peak (Fig. 20) to the right along the abscissa. The overall effect is a higher temperature. This explanation does not indicate any violation of the second law of thermodynamics: all heat in the system is eventually conducted away.

It appears then that, under the circumstances described, the advancing ice/water interface acquires properties very similar to that of Maxwell's demon.

The greatest difficulty with the above explanation resides in the great uncertainty in understanding the liquid state in general, and the structure of water in particular (Eisenberg and Kauzman 1969). It is therefore possible that the hypothesis presented may turn out to be concise, intriguing and wrong.

LITERATURE CITED

- Bakaiev, V.A., V.F. Kiselev and K.G. Krasil'nikov (1959) Ice melting temperature lowering in the capillaries of a porous body. In *Physical Chemistry* (in Russian), Doklady, USSR Academy of Science, vol. 125, no. 4.
- Ben-Naim, Arien (1974) *Water and aqueous solutions*. New York: Plenum Publishing House.
- Dalla-Valle, Jr., M. (1948) *Micromeritics*. New York: Pitman Publishing Corp.
- Dersievicz, H. (1958) Mechanics of granular matter. In *Advances in Applied Mechanics*. New York: Academic Press, Inc.
- Dorsey, N.E. (1948) The freezing of supercooled water. In *Transactions of the American Philosophical Society*, vol. 38, no. 3.
- Eisenberg, D. and W. Kauzman (1969) *The structure and properties of water*. Oxford: Oxford University Press.
- Green, H.S. (1952) *Molecular theory of fluids*. Amsterdam: North Holland Publishers.
- Loeb, L.B. (1962) *The kinetic theory of gases* (in German). Berlin: Springer Verlag.
- Vanderwilt, J.W. (1938) Improvements in the polishing of ores. *Economic Geology*, vol. 25, p. 307.